Polymerization Studies of Halogenated, Unsaturated Quaternary Ammonium Salts

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TABLE OF CONTENTS

		Page
LIST OF TABLES		iii
LIST OF ILLUSTRATIONS		iv
PREFACE		v
Section		
I.	INTRODUCTION	1
	A. Historical Notes B. Statement of the Problem C. Source and Purification of Reactants D. General Remarks	
II.	PREPARATION OF UNSATURATED TERTIARY AMINES	6
	A. General Discussion B. Ammonium Hydroxide Syntheses C. Syntheses Using Primary and Secondary Amines	
III.	UNSATURATED QUATERNARY AMMONIUM COMPOUNDS	20
	A. General Discussion B. Experimental	
IV.	POLYMERIZATION OF QUATERNARY AMMONIUM HALIDES	29
	A. Discussion B. Experimental	
V.	ION EXCHANGE CAPACITY OF RESINS	41
	A. General Considerations B. Experimental	
VI.	RATE OF ION EXCHANGE OF RESINS	51
	A. General B. Experimental	

TABLE OF CONTENTS (Continued)

Section		Page
VII.	EVALUATION OF RESINS	57
VIII.	METHODS OF ANALYSIS	59
IX.	DISCUSSION OF RESULTS	61
X.	SUMMARY	64
BIBLIOGRAPHY		66
ACKNOWLEDGMENTS		68
BIOGRAPHICAL ITEMS		69

LIST OF TABLES

Table		Page
I.	Physical Properties of Unsaturated Tertiary Amines . .	18
II.	Analytical Data, Unsaturated Tertiary Amines	19
III.	Unsaturated Quaternary Ammonium Halides.	28
IV.	Properties of Ion Exchange Resins.	40

LIST OF ILLUSTRATIONS

Graph		Page
I.	Ion Exchange Capacity Titration of Poly-Triallyl, 2-Chloroallyl Ammonium Bromide	46
II.	Effect of Temperature of Polymerization on the Capacity of the Resin.	47
III.	Ion Exchange Capacity Titrations of Suspension Polymers	48
IV.	Comparison of Capacities of Suspension and Bulk Polymers Prepared at 40°C.	49
V.	Effect of Initial Concentration of the Anion on the Capacity of the Resin.	50
VI.	Relationship Between the Concentration of the Anion in the Effluent and Volume of Effluent Passed. . . .	56

PREFACE

The research presented in this dissertation was carried out under the sponsorship of the Office of Naval Research.

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Section I

INTRODUCTION

A. Historical Notes

The significance of ion exchange has far exceeded any predictions that could have been made when it was first observed by J. Thomas Way in 1850.[24] Way found that certain soils had the ability to absorb the ions present in soluble fertilizers, giving up, in turn, ions already present in the soil. While this discovery was of great importance in the study of soils, it has led to a variety of applications in industry and research that completely overshadow its original significance.

The first industrial application of ion exchange was made possible early in the twentieth century when natural and artificial zeolites (aluminosilicates) were found applicable as water softeners by Gans.[8] This marked the beginning of a period of intensive research in the development of new and better cation exchange substances. Among these new substances, sulfonated coals and synthetic resins were outstanding.

The first extension of ion exchange study to include anions may be credited to the work of Adams and Holmes in 1935.[2] In addition to producing synthetic cation exchange substances, they developed a resin capable of exchanging anions by means of the condensation of polyamines with formaldehyde. It was then, for the first time, that ion-free water could be obtained without resorting to distillation.

The discovery of Adams and Holmes led to the production of other resins from amines and formaldehyde by Kirkpatrick[13] and others. Kirkpatrick selected m-phenylenediamine as a reactant. In this case, the gel produced was broken up and dried at 115°C. to reduce its solubility in water. Other aromatic amines were employed in this condensation, among them, aniline, m-toluidine, and sym. m-xylidine.[1,9,18] It was found that all resins so produced were weakly basic, and therefore incapable of removing certain anions from solution. In order to enhance this basicity, substituted groups were employed, such as methyl, ethyl, cyano,[10] phenolic hydroxyl, N-substituted alkylene, hydrazine,[9] and others. Anion exchanging resins were also produced by other aldehyde condensations with melamine,[3,6] polyalkylene polyamines,[17] guanidine derivatives,[23] methylol-forming phenols, and non-aromatic amines with at least one hydrogen atom on the nitrogen atom.[21] Further work involving the heating of hydrocarbon dihalides with ammonia in a closed vessel produced satisfactory exchange resins.[7]

Among the most basic anion exchange resins on the market at present are Nalcite A-2[a] and Amberlite IRA 400.[b] Polytetraallyl ammonium bromide and other polyquaternary ammonium halides, produced in these laboratories,[5] compare favorably with these commercial polymers in basicity but have lower ion exchange capacities per unit volume. These

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(a) A product of National Aluminate Corp., Chicago, Ill.

(b) A product of The Resinous Products and Chemical Co., Philadelphia, Pa.

resins were made by the peroxide-catalyzed polymerization of unsaturated quaternary ammonium halides. The resins were broken up into granules by leaching with hot water and were dried at 100°C.

Anion exchange resins have found many important industrial uses in addition to the purification of water. Among these are the recovery of metals,[19,22] the recovery of tartrates from grape wastes,[16] and the manufacture of dextrose. Excellent discussions of the progress and applications of anion exchange may be found in Industrial and Engineering Chemistry.[11,14]

A brief discussion of the physical make-up of the resin particle is considered in order here. It is believed that this particle consists of a large network of long chain polymer units, tied together in three dimensions by crosslinking. The hydroxyl form of the particle has hydroxyl groups associated with each active atom (nitrogen). When this particle is wet, swelling occurs, extending the size of the structure as far as crosslinking permits. The hydroxyl ions are then able to move freely within the particle and around its immediate periphery. The ions cannot migrate away from the particle entirely, since they are held by the electrical charge of the particle. Thus, in effect, a layer of hydroxyl ions is always present on the surface of the particle. This concept has been substantiated by the work of Jenny,[12] who found that the finely divided hydroxyl form of the resin could be made to give a pH increase when stirred around a glass electrode.

B. Statement of the Problem

The absence of anion exchange resins of high basicity led Butler and Bunch[4,5] to investigate the polymerization of various unsaturated quaternary ammonium compounds with peroxide catalysts. They succeeded in preparing resins capable of operating in a pH range of 11 to 12, but having capacities no greater than 0.40 milliequivalents of anion per milliliter of wet resin. It was believed by this observer that this low capacity was caused in part by the relatively low density of the resin particles.

With this in view, this investigation was directed toward producing resins of higher capacity by use of halogenated quaternary ammonium halides as monomers and by varying the conditions and methods of polymerization.

C. Source and Purification of Reactants

The diallylamine and dichloropropenes used in this work for the preparation of unsaturated tertiary amines were obtained from Shell Chemical Company. The diallylamine was used as received, but the 2,3-dichloropropene-1 was fractionated, recovering the fraction boiling in the range of 93-95°C. The 1,3-dichloropropene-1 was fractionated to separate the *cis* and *trans* isomers. The *cis* isomer boiled in the range of 103.5-104.5°C.; the *trans* isomer, in the range of 112-113°C.

The piperidine was obtained from Eastman Kodak Company, and the morpholine from Carbide and Carbon Chemical Company. Both were used

without further purification. The allyl bromide was a product of Dow Chemical Company and was used without fractionation. The tertiary butyl hydroperoxide was obtained as a 60% solution from Union Bay State Company.

D. General Remarks

All amines prepared herein were fractionated through a 2 x 82 cm. heated column packed with Raschig rings. The pot heat was applied by means of Glas-Col heating mantles. Temperatures recorded are uncorrected. Pressures lower than atmospheric were determined by means of a Zimmerli Gauge.

Densities were determined by means of a calibrated 10 ml. Kimble specific gravity bottle, equipped with a standard taper thermometer. Refractive indexes were found by use of an Abbe Refractometer. These two physical constants were determined at 25° C.

Section II

PREPARATION OF UNSATURATED TERTIARY AMINES

A. General Discussion

It was necessary to prepare unsaturated tertiary amines as intermediates for the preparation of the quaternary ammonium compounds. Two methods were used: The ammonium hydroxide synthesis and the method described by Willson and Wheeler,[20] as modified by Butler and Bunch.[5] The former method was used to prepare amines with three like groups on the nitrogen atom, while the latter method was applicable when appropriate secondary amines were available.

B. Ammonium Hydroxide Syntheses

1. General

This method was used for the preparation of triallyl amine (previously reported) and tri-(2-chloroallyl) amine. Ammonium hydroxide — a large excess over the theoretical requirement — was added to a two-liter, three-necked flask equipped with a mechanical stirrer, cold water reflux condenser, and addition funnel. Sufficient water was added so that the solubility of ammonia in water at 100°C. was not exceeded. The flask was then heated to 70-100°C. and the appropriate halide added dropwise with vigorous stirring. After addition of the halide had been completed, the stirring and heating were continued for 3-10 hours. After this period, the flask was cooled and the amines were salted out by means of the

addition of solid sodium hydroxide. It was found necessary to cool the reaction mass in an ice bath during this salting out process. The amine layer was removed by means of a separatory funnel. Steam distillation and subsequent salting out of the distillate did not prove profitable, since virtually all of the amine was removed by the first addition of sodium hydroxide. The impure amine was dried overnight over solid sodium hydroxide and fractionated.

A heated column, 2 x 82 cm., equipped with an insulating jacket and column thermometer and packed with Raschig rings, was used for the fractionation. The average reflux ratio used was 1:10, with the column temperature within five degrees of the head temperature. A pot thermometer was employed so that overheating of the product could be avoided. To further reduce decomposition, the distillation pressure was reduced, when necessary, so that the boiling points of most of the amines fell below 100°C.

The procedure outlined above had the disadvantage of producing primary amines, secondary amines, and [it is presumed] some quaternary ammonium compounds as by-products. However, reasonably high yields of the tertiary amines were obtained. In some cases, the by-products of the reaction were useful in other syntheses.

The physical constants, molar refractions, analyses, and yields of the tertiary amines produced by this method of synthesis may be found in Tables I and II, following the experimental section.

2. Experimental

Synthesis of Triallyl Amine:

$$CH_2=CH-CH_2-N(-CH_2-CH=CH_2)-CH_2-CH=CH_2$$

A mixture of 273.6 g. of concentrated ammonium hydroxide and 1050 ml. of water was added to the reaction flask and heated to 75-80°C. with an electrical heating mantle. The solution was stirred vigorously with a mechanical stirrer during the dropwise addition of 363 g. (3 moles) of allyl bromide. After this addition had been completed, the temperature was maintained and the stirring continued for 3 hours. The reaction mass was then cooled in an ice bath during the addition of solid sodium hydroxide (enough to saturate the solution). The supernatant layer, a mixture of allyl, diallyl, and triallyl amines, was separated, dried for 18 hours over solid sodium hydroxide, and fractionated through the column described previously. The primary and secondary amines, recovered in small quantities, were discarded. A total of 30.6 g. of triallyl amine was collected, boiling in the range of 149-155°C. at 760 mm. This quantity represents a yield of 22.3% of the theoretical. Since triallyl amine has been reported previously, it was characterized by means of its physical constants.

Synthesis of Tri-(2-chloroallyl) Amine:

$$CH_2=CCl-CH_2-N(-CH_2-CCl=CH_2)-CH_2-CCl=CH_2$$

A mixture of 90.2 g. of concentrated ammonium hydroxide and 350 ml. of water was heated to 100° C. in a one-liter, three-necked flask. One hundred eleven grams (1 mole) of 2,3-dichloropropene-1 was added dropwise, with vigorous stirring. The mixture was then held at 100° with continued stirring for 8 hours, cooled, and allowed to separate. The heavy, oily layer which settled out was removed and the remaining aqueous layer saturated with solid sodium hydroxide. No significant quantity of amine separated as a result of this salting out. The amine mixture was dried overnight over solid sodium hydroxide and fractionated under reduced pressure. The quantities of primary and secondary amines produced were negligible, so these compounds were discarded. A total of 58.9 g. of tri-(2-chloroallyl) amine was recovered, boiling in the range of 120-121.5°C. at 9-10 mm., and representing a yield of 73.5% of the theoretical.

Physical Constants:

n_D^{25} 1.5036

D_4^{25} 1.1868

B.p..... 120-121.5° at 9-10 mm.

Nitrogen Analysis:

Calculated..... 5.82%
Observed..... 5.89%

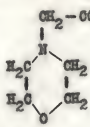
C. Syntheses using Primary and Secondary Amines

1. General

For the remainder of the tertiary amines prepared in this research, primary or secondary amines were used as starting materials instead of ammonium hydroxide. The method, as described by Butler and Bunch,[5] involved the reaction of the appropriate halide with a thin paste of the primary or secondary amine and sodium bicarbonate in water. The reaction was carried out in a round-bottomed, three-necked flask of suitable capacity equipped with a mechanical stirrer, cold water reflux condenser, and dropping funnel. The reaction mixture was heated to 100°C. by means of a steam bath throughout the reaction time. Vigorous stirring was maintained during and after the addition of the halide. The total time of each reaction was about 6 hours. After this period, the reaction mass was cooled and saturated with solid sodium hydroxide as described previously. The amine layer was separated, dried over solid sodium hydroxide, and distilled. In order to avoid excessive decomposition, all of the amines prepared were fractionated under reduced pressure and subsequently stored in a refrigerator. Physical constants and analytical data were obtained, using freshly distilled samples. Yields of tertiary amines obtained by this method were good, usually above 70%. The reaction had the further advantage of giving practically no side products, making purification an easy matter. The amines produced were all colorless, mobile liquids, turning yellow slowly when exposed to light.

2. Experimental

Synthesis of N-2-Chloroallyl Morpholine:



Forty-three and one-half grams (0.5 mole) of morpholine and 42 g. of sodium bicarbonate were mixed in a 500 ml., three-necked flask with sufficient water to form a thin paste. The mixture was heated to 100°C. with a steam bath and stirred while 61.1 g. (0.5 mole plus 10% excess) of 2,3-dichloropropene-1 was added dropwise. The reaction was continued for 5 hours at reflux, and then the reaction mixture was cooled. The amine layer was removed and the aqueous layer saturated with solid sodium hydroxide, giving further separation of the product. The crude amine was dried and fractionated under reduced pressure. A total of 71.7 g. of material boiling in the range of 99-101°C. at 26 mm. was collected, representing a yield of 88.7%.

Physical Constants:

n_D^{25} 1.4796

d_4^{25} 1.0887

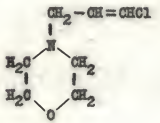
B.p. .....99-101° at 26 mm.

Nitrogen Analysis:

Calculated..... 8.67%

Observed..... 8.49%

Synthesis of N-cis 3-Chloroallyl Morpholine:



Forty-three and one-half grams (0.5 mole) of morpholine was mixed with 42.0 g. of sodium bicarbonate and enough water to form a thin paste. The mixture was heated to 100° C. in a 500 ml., three-necked flask and stirred vigorously during the dropwise addition of 61.1 g. (0.5 mole plus 10% excess) of cis 1,3-dichloropropene-1. After the addition had been completed, the mixture was heated and stirred for 7 hours — then cooled. The product was salted out of the reaction mass by saturation with solid sodium hydroxide, dried, and fractionated. A yield of 57.4 g. of product was recovered, boiling in the range of 109-110°C. at 26 mm. This represented 71.0% of the theoretical.

Physical Constants:

n_D^{25} 1.4866

D_4^{25} 1.0967

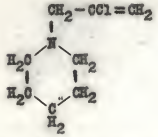
B.p.....109-110° at 26 mm.

Nitrogen Analysis:

Calculated.....8.67%

Observed.....8.61%

Synthesis of N-2-Chloroallyl Piperidine:



Twenty-eight and four-tenths grams (0.33 mole) of piperidine and 35 g. of sodium bicarbonate were mixed in a 500 ml., three-necked flask with enough water to give a thin paste. The mixture was heated to 100° on the steam bath, stirring was begun, and 40.7 g. (0.33 mole plus 10% excess) of 2,3-dichloropropene-1 added dropwise. Heating and stirring were continued for 6 hours after the addition had been completed. The reaction mass was then cooled and the amine salted out with solid sodium hydroxide. Upon drying and distilling, 37.8 g. of product was obtained, boiling in the range of 70-71°C. at 10 mm. This quantity represented a yield of 71.0% of the theoretical.

Physical Constants:

n_D^{25} 1.4767

D_4^{25} 0.9969

B.p..... 70-71° at 10 mm.

Nitrogen Analysis:

Calculated..... 8.78%

Observed..... 8.74%

Synthesis of Diallyl, 2-Chloroallyl Amine:

$$CH_2=CH-CH_2-N(-CH_2-CH=CH_2)-CH_2-CCl=CH_2$$

Forty-eight and six-tenths grams (0.5 mole) of diallyl amine was mixed with 42.0 g. of sodium bicarbonate and water to produce a paste and added to a 500 ml., three-necked flask. After heating to 100°, 61.1 g. (0.5 mole plus 10% excess) of 2,3-dichloropropene-1 was added dropwise, with stirring. The reaction was then continued for 5.5 hours and the crude product separated as described previously. The amine was then dried and fractionated under reduced pressure. A total of 51.7 g. of product was collected, boiling in the range of 81-82°C. at 19-20 mm. This quantity represented a yield of 60.4%.

Physical Constants:

n_D^{25} 1.4680

D_4^{25} 0.9394

B.p.....81-82° at 19-20 mm.

Nitrogen Analysis:

Calculated..... 8.16%

Observed..... 8.16%

Synthesis of Methyl, Di-(trans 3-Chloroallyl) Amine:

$$ClCH=CH-CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2-CH=CHCl$$

A mixture of 130 ml. of a 25% solution of methyl amine (slightly more than 1 mole) and 168 g. of sodium bicarbonate was added to a 1-liter, three-necked flask with enough water to produce a paste. The temperature of the mixture was raised to 100°C., and 222 g. (2 moles) of trans 1,3-dichloropropene-1 was added dropwise, with vigorous agitation. The reaction was continued for 4 hours after this addition. After this period, the reaction mixture was cooled and the amine salted out with solid sodium hydroxide. The crude product was dried and fractionated under reduced pressure. The fraction boiling at 94-95°C. at 10 mm. was collected, having a total weight of 59.1 g. and representing a yield of 32.8%.

Physical Constants:

n_D^{25} 1.4910

D_4^{25} 1.1069

B.p. .....94-95° at 10 mm.

Nitrogen Analysis:

Calculated.....7.78%

Observed.....7.74%

Synthesis of Allyl, Di-(2-Chloroallyl) Amine:

$$CH_2=CCl-CH_2-N(CH_2=CH-CH_2)-CH_2-CCl=CH_2$$

Twenty-eight and one-half grams (0.5 mole) of allyl amine was mixed with 84.0 g. of sodium bicarbonate and water to make a paste and placed in a 500 ml., three-necked flask. The mixture was heated to 100° C. and stirred during the dropwise addition of 122.1 g. (1 mole plus 10% excess) of 2,3-dichloropropene-1. The reaction was continued for 6 hours, after which the crude amine was salted out as described previously. The product was dried and distilled under reduced pressure, boiling at 88.5°C. at a pressure of 5.6 mm. The yield of product was 22.7 g., or 22.0% of the theoretical.

Physical Constants:

n_D^{25} 1.4863

D_4^{25} 1.0692

B.p.....88.5° at 5.6 mm.

Nitrogen Analysis:

Calculated..... 6.80%

Observed..... 6.75%

Synthesis of Diallyl, trans 3-Chloroallyl Amine:

$$CH_2=CH-CH_2-N(CH_2-CH=CH_2)-CH_2-CH=CHCl$$

Forty-eight and six-tenths grams (0.5 mole) of diallyl amine was mixed with 63 g. of sodium bicarbonate and water in a 500 ml., three-necked flask. The mixture was heated to 80°C. and stirred during the dropwise addition of 61.1 g. (0.5 mole plus 10% excess) of trans 1,3-dichloropropene-1. The heating and stirring were continued for a period of 6 hours after addition of the halide had been completed. The reaction mixture was then cooled and saturated with sodium hydroxide to salt out the crude amine. Fractionation of the dry, crude product produced 46.2 g. of amine, boiling in the range of 66-67°C. at 3.9 mm. This quantity represented a yield of 54.0% of the theoretical.

Physical Constants:

n_D^{25} 1.4748

D_4^{25} 0.9477

B.p. .....66-67° at 3.9 mm.

Nitrogen Analysis:

Calculated..... 8.16%

Observed..... 8.11%

TABLE I

PHYSICAL PROPERTIES OF UNSATURATED TERTIARY AMINES

Compound	B.P.,		n_D^{25}	d_4^{25}	R,		Yield, %
	C.	Mm.			Calculated	Observed	
N-2-Chloroallyl Morpholine	99-101	26	1.4796	1.0887	42.31	42.15	88.7
N-cis 3-Chloroallyl Morpholine	109-110	26	1.4866	1.0967	42.31	42.36	71.0
N-2-Chloroallyl Piperidine	70- 71	10	1.4767	0.9969	45.28	45.23	71.0
Diallyl, 2-Chloroallyl Amine	81- 82	19.2-19.6	1.4680	0.9394	51.17	50.80	60.4
N-trans 3-Chloroallyl Morpholine	91- 92	8.5	1.4869	1.0973	42.31	42.36	82.6
Tri-(2-Chloroallyl) Amine	120-121.5	9.3	1.5036	1.1868	60.90	60.00	73.5
Methyl, Di-(trans 3-Chloroallyl) Amine	94- 95	10	1.4910	1.1069	47.27	47.12	32.8
Allyl, Di-(2-Chloroallyl) Amine	88.5	5.6	1.4863	1.0692	56.04	55.38	22.0
Diallyl, trans 3-Chloroallyl Amine	66-67	3.9	1.4748	0.9477	51.17	50.98	54.0

TABLE II

ANALYTICAL DATA, UNSATURATED TERTIARY AMINES

Compound	Empirical Formula	Nitrogen, %	
		Calculated	Observed
N-2-Chloroallyl Morpholine	$C_7H_{12}ClNO$	8.67	8.49
N-*cis* 3-Chloroallyl Morpholine	$C_7H_{12}ClNO$	8.67	8.61
N-2-Chloroallyl Piperidine	$C_8H_{14}ClN$	8.78	8.74
Diallyl, 2-Chloroallyl Amine	$C_9H_{14}ClN$	8.16	8.16
N-*trans* 3-Chloroallyl Morpholine	$C_7H_{12}ClNO$	8.67	8.63
Tri-(2-Chloroallyl) Amine	$C_9H_{12}Cl_3N$	5.82	5.89
Methyl, Di-(*trans* 3-Chloroallyl) Amine	$C_7H_{11}Cl_2N$	7.78	7.74
Allyl, Di-(2-Chloroallyl) Amine	$C_9H_{13}Cl_2N$	6.80	6.75
Diallyl, *trans* 3-Chloroallyl Amine	$C_9H_{14}ClN$	8.16	8.11

Section III

UNSATURATED QUATERNARY AMMONIUM COMPOUNDS

A. General Discussion

The quaternary ammonium halides investigated in this research were prepared by the method described by Butler and Bunch.[4,5] The procedure consisted of adding an excess of the appropriate unsaturated halide to an acetophenone solution of the unsaturated tertiary amine. Although some quaternary ammonium compounds formed very readily at room temperatures, it was found desirable to reflux the mixture for several hours to increase the yield of the product. This practice was carried out in all cases. In some instances, a quantity of the crystalline quaternary ammonium compound separated upon cooling the reaction mixture. This first crop of crystals was recovered by filtration, and a second crop was produced by the addition of dry ether to the mother liquor. Some of the quaternary salts prepared in this work were sufficiently soluble in the amount of acetophenone used to require the addition of ether to produce the first crystals. The crude products were purified by repeated recrystallization from alcohols, acetone-ether, or chloroform-ether mixtures. Speed in filtration and handling of the products was essential, since most of the compounds were very hygroscopic in the impure state. Ether which had been dried over sodium was used to precipitate the products.

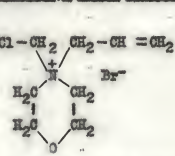
Of the compounds prepared in this phase of the investigation, the quaternary halide produced from the reaction of allyl bromide with cis 3-chloroallyl morpholine was not recovered as a solid. This reaction led uniformly to a very viscous liquid of a taffy-like consistency. Attempts to obtain the crystalline compound by recrystallizing from a variety of solvents proved fruitless. The crude product was subjected to rather strenuous methods of dehydration, such as maintaining it under a pressure of 0.1 mm. at a temperature of 100°C. for several days; however, no crystallization occurred. The trans isomer of this quaternary proved almost as refractory toward crystallization, but after the rigorous dehydration described above and storage at 5°C. for several weeks, a small crop of crystals was obtained. The quantity recovered was enough for analysis but insufficient to justify further attempts of purification. The reasons for such difficulties in obtaining solid compounds are unknown, but it is presumed that supercooled liquids were produced which contained small amounts of water and other impurities.

The remaining unsaturated quaternary ammonium salts prepared herein were white, crystalline solids, very soluble in water, acetone, and alcohol and insoluble in ether. The products were stored in vacuum desiccators to prevent absorption of moisture.

The analyses, yields, and melting points of the unsaturated quaternary ammonium halides studied in this work may be found in Table III, following the experimental section.

B. Experimental

Synthesis of N-2-Chloroallyl, N-Allyl Morpholinium Bromide:



Forty and four-tenths grams (0.25 mole) of N-2-chloroallyl morpholine was mixed with 100 ml. of redistilled acetophenone in a 500 ml., three-necked flask equipped with a reflux condenser (ice water), addition funnel, and mechanical stirrer. The mixture was heated to 100°C., with stirring, during the dropwise addition of 31.7 g. (an excess over 0.25 mole) of allyl bromide. After refluxing for 6 hours, a considerable amount of quaternary halide had separated. This was removed by filtration, and a second crop was recovered from the mother liquor by the addition of dry ether. The crude product was freed of ether-soluble impurities by means of a Soxhlet extractor and then recrystallized from absolute alcohol by addition of dry ether. Twenty-one grams of quaternary, representing a yield of 29.7%, was recovered.

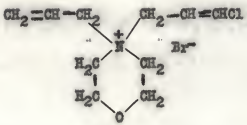
Melting Point..... 171-172°C.

Bromine Analysis:

Calculated.....28.28%

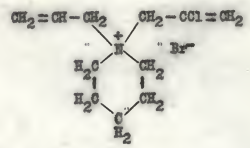
Observed.....28.41%

Synthesis of N-Allyl, N-cis 3-Chloroallyl Morpholinium Bromide:



Forty and four-tenths grams (0.25 mole) of N-cis 3-chloroallyl morpholine was mixed with 100 ml. of acetophenone in a 500 ml. flask equipped as described previously. The mixture was heated to 100°C. and stirred during the dropwise addition of 31.7 g. (an excess over 0.25 mole) of allyl bromide. The reaction was continued for 6 hours with no evidence of insoluble material. Since cooling of the mixture to 0°C. failed to produce a solid, a quantity of dry ether was added. At this point, a very viscous, brown liquid separated. Attempts to obtain a crystalline solid from this substance by means of recrystallization from several solvents were futile. The liquid mass was thoroughly extracted with ether and held under vacuum (0.1 mm.) at a temperature of 100°C. for several days. The product was then stored at 5°C. for several weeks without the appearance of crystals. The product showed the typical properties of a quaternary ammonium halide in its solubility in water and in the possession of an ionic halogen atom. Since a pure compound could not be isolated, the identity of this quaternary ammonium halide was not proved by analysis, but rather was only assumed on the basis of the method of preparation. A total of 46.1 g., representing an approximate yield of 65.2%, was collected.

Synthesis of N-Allyl, N-2-Chloroallyl Piperidinium Bromide:



Thirty-two grams (0.2 mole) of N-2-chloroallyl piperidine was mixed with 80 ml. of acetophenone in a 200 ml., three-necked flask equipped as described previously. The mixture was heated on a steam bath and 25.4 g. (0.2 mole plus 5% excess) of allyl bromide added dropwise, with vigorous stirring. The reaction was continued for 6 hours under reflux, during which time a granular solid separated and the solution turned dark red in color. The solid material was removed by filtration and a second crop recovered by the addition of dry ether to the mother liquor. The crude product was washed free of colored, ether-soluble materials by extraction with ether in a Soxhlet extractor and then was further purified by recrystallization from alcohol with dry ether. A total of 50.8 g. of white, crystalline material was collected, representing a yield of 90.5%.

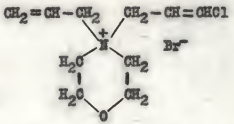
Melting Point..... 163-164°C.

Bromine Analysis:

Calculated.....28.48%

Observed.....28.47%

Synthesis of N-Allyl, N-trans 3-Chloroallyl Morpholinium Bromide:



Forty and four-tenths grams (0.25 mole) of N- trans 3-chloroallyl morpholine was mixed with 100 ml. of acetophenone in a 500 ml., three-necked flask, equipped as described before. The mixture was heated to 100°C. on the steam bath and stirred during the dropwise addition of 31.8 g. (0.25 mole plus 5% excess) of allyl bromide. The reaction was continued for 6 hours under reflux. At the end of this time, a viscous mass had separated. This substance was washed free of ether-soluble impurities and dissolved in absolute alcohol. Upon addition of dry ether, the viscous liquid again appeared. Further attempts to form crystals by recrystallization from chloroform, acetone, and other solvents failed. The product was then dried under vacuum and stored for several weeks at 5°C., as was done with the cis isomer [p.23]. A small amount of crystalline material was collected and analyzed. The total weight of impure quaternary was 47.6 g., representing an approximate yield of 67.4%.

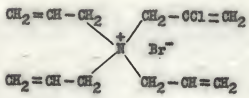
Melting Point.....160-165°C.

Bromine Analysis:

Calculated..... 28.28%

Observed..... 27.90

Synthesis of Triallyl, 2-Chloroallyl Ammonium Bromide:



Forty-two and nine-tenths grams (0.25 mole) of diallyl, 2-chloroallyl amine was mixed with 100 ml. of acetophenone in a 500 ml., three-necked flask, equipped as described before. After heating to 100°C., 31.8 g. (0.25 mole plus 5% excess) of allyl bromide was added dropwise, with stirring. At the end of 8 hours, no solid material had separated, so the reaction mixture was chilled to 0°C., with vigorous stirring. The crystals which formed were filtered and washed with dry ether. A second crop of crystals was obtained by adding ether to the mother liquor. The two crops of crystals were combined and recrystallised from alcohol with ether. A total weight of 20.6 g. was collected, representing a 28.2% yield of the theoretical.

Melting Point..... 155-160°C.

Bromine Analysis:

Calculated..... 27.31%

Observed..... 27.25%

Synthesis of Butyl, Diallyl, trans 3-Chloroallyl Ammonium Chloride:

Seventy-six and six-tenths grams (0.5 mole) of butyl diallyl amine was mixed with 50 ml. of acetophenone in a 500 ml., three-necked flask, as described previously. The mixture was heated to 100°C., and 61.0 g. (0.5 mole plus 10% excess) of trans 1,3-dichloropropene-1 was added dropwise, with stirring. After 9 hours, a viscous liquid separated but would not crystallize when chilled. Addition of ether to the reaction mixture, however, caused the formation of considerable solid material which formed a nucleus for the crystallization of the entire sample. The product was filtered, washed free of reactants, and recrystallized from alcohol. A yield of 111.7 g., representing 84.5% of the theoretical, was obtained.

Melting Point..... 146-149°C.

Chlorine Analysis:

(Ionizable)

Calculated.....13.42%

Observed.....13.38%

TABLE III

UNSATURATED QUATERNARY AMMONIUM HALIDES

Compound	Empirical Formula	Ionic Halogen			M. p., (°C.)	Yield, %
		Element	Calculated, %	Observed, %		
N-2-Chloroallyl, N-Allyl Morpholinium Bromide	$C_{10}H_{17}BrClNO$	Br	28.28	28.41	171-172	29.7
N-Allyl, N-cis 3-Chloroallyl Morpholinium Bromide	$C_{10}H_{17}BrClNO$	Br	28.28	...[a]	...[a]	65.2
N-Allyl, N-2-Chloroallyl Piperidinium Bromide	$C_{11}H_{19}BrClN$	Br	28.48	28.47	163-164	90.5
N-Allyl, N-trans 3-Chloroallyl Morpholinium Bromide	$C_{10}H_{17}BrClNO$	Br	28.28	27.90	160-165[b]	67.4
Triallyl, 2-Chloroallyl Ammonium Bromide	$C_{12}H_{19}BrClN$	Br	27.31	27.25	155-160	28.2
Butyl, Diallyl, trans 3-Chloroallyl Ammonium Chloride	$C_{13}H_{23}Cl_2N$	Cl	13.42	13.38	146-149	85.5

(a) No crystals were obtained.

(b) Compound recrystallized only once.

Section IV

POLYMERIZATION OF QUATERNARY AMMONIUM HALIDES

A. Discussion

Polymerization is divided into two general classifications -- condensation and addition. The point of difference between these two classes lies in the fact that the former is always accompanied by the production of some simple molecule as a by-product, such as water, ammonia, or sodium chloride; while the latter class gives no by-products. The polymer unit formed by addition polymerization has the same empirical formula as the original monomer. An example of addition polymerization is found in the peroxide-catalyzed polymerization of certain compounds with unsaturated carbon-to-carbon linkages. The polymerization of unsaturated quaternary ammonium compounds performed in this research belongs to this type of addition polymerization.

The nature of the polymer obtained is known to vary with the functionality of the monomer. If the monomer has a functionality of two (for example, a double bond), a linear polymer results, being thermoplastic and more or less soluble. However, if the functionality is increased, the possibility of crosslinking appears, resulting in a thermosetting polymer, insoluble in ordinary solvents. The extent of crosslinking may be quite variable, depending upon the conditions employed, giving a wide range of solubility of the product. This solubility may extend from gel formation in those cases in which the degree of crosslinking is low to complete insolubility and merely swelling in those cases in which crosslinking is more extensive. Very little swelling in the presence of solvents may

finally occur when a highly crosslinked polymer is obtained. For this reason, the amount of swelling produced when the polymer is immersed in a solvent may sometimes be used as a rough measure of the extent of crosslinking.

In this study of ion exchange resins, polyfunctional monomers were employed, since a high degree of crosslinking (low solubility) was desired. The functionality ranged from four (molecules containing two double bonds) to eight (molecules containing four double bonds).

Many factors are recognized as significant in determining the quality of anion exchange resins. Among the factors considered were: (1) The nature of the monomer, (2) The nature of the catalyst, (3) The concentration of the catalyst, (4) The presence of a solvent, (5) The temperature of polymerization, (6) The time of polymerization, and (7) The mechanical conditions under which the polymerization was carried out. These factors will be considered in order.

The purpose of this investigation was to develop an anion exchange resin of higher capacity than those produced previously from similar monomers. Since the capacity of these resins often is based upon a standard volume of the wet resin, it was believed that any method producing a denser particle (giving more active groups per unit volume) would tend to increase the capacity of the resin. For this reason, halogenated quaternary ammonium halides were studied as monomers. Polymerization of these substances was carried out at various temperatures, holding all other factors constant. For a more or less complete study of the polymerization conditions, tetrallyl ammonium bromide was used, since it was most easily obtained.

The catalyst used in all of these polymerization experiments was tertiary butyl hydroperoxide. This catalyst was found to work better than others with quaternary ammonium halides by Butler and Bunch.[4,5]

Since a large proportion of the catalyst has a tendency to give a relatively low molecular weight polymer, the concentration was held constant at about 1.6% throughout these experiments.

A small amount of water was added to the monomers in all polymerization systems. This water had the double effect of lowering the melting point of the monomer and of dissolving it, giving the necessary liquid system. Strictly speaking, polymerization with the use of solvents is considered solution polymerization, but since such a small proportion of water was used, the term "bulk polymerization" is used herein for such systems. About 5% by weight of water was added to the monomer for all bulk polymerization studies.

Since a low temperature is known to be favorable for the formation of higher molecular weight polymers, it was believed that a resin of lower solubility [i.e., one with less tendency to swell when wet] could be obtained by carrying out the polymerization reactions in the range of room temperature. In order to investigate the effect of the temperature on the quality of the product, reactions were carried out at 65°, 40°, 30°, and 23° C. For this study, only tetrallyl ammonium bromide was used.

The time permitted for complete polymerization in all cases was selected arbitrarily. An attempt was made to allow ample time for the

reaction to proceed to completion in each case. For the reactions in which the first evidence of polymerization appeared within an hour, a 24-36 hour period was allowed to effect completion of the reaction. When as much as 12 hours elapsed before polymerization began, a 7-14 day period was permitted.

The most obvious mechanical means of conducting these polymerization experiments was in bulk; that is, by mixing the monomer with the catalyst and enough water to give a liquid system and allowing polymerization to take place. This method led to hard, glassy solids in one piece. The solids were then broken up by leaching with water. With this method, the size of the particle could not be controlled, since it was determined only by the distribution of unreacted (water-soluble) monomer mixed with the polymer. It was believed that a technique of emulsion, or suspension polymerization, in which an insoluble second phase was introduced and stirring employed, might lead to better control of the particle size and perhaps of particle density. In order to investigate the effect of mechanical handling on the quality of the polymer, tetrallyl ammonium bromide was polymerized in bulk, in emulsion, and in suspension.

B. Experimental

1. Bulk Polymerization

These experiments were carried out using the monomers listed below.

Allyl, 2-Chloroallyl Morpholinium Bromide:— Polymerization of this compound was attempted at three different temperatures: 85°, 65°, and 30° C. In each case, a mixture of 10 g. of the quaternary ammonium halide, 0.57 g. of water, and 0.17 g. of catalyst was maintained at the selected temperature until the reaction was presumed to be complete. The temperature was held constant in the experiments conducted at 85° and 65°, by means of an electric oven, for a period of 24 hours. At the end of this time the polymers had assumed a hard, glass-like consistency and were light brown in color. These polymers were found to be completely soluble in water, showing little crosslinking. The third sample was maintained at 30° in a constant temperature bath for 7 days. This resin was likewise soluble in water.

The soluble polymers resulting from this monomer were obviously unsatisfactory as ion exchange resins because of their solubility.

Allyl, trans 3-Chloroallyl Morpholinium Bromide.— In this case, the crude product obtained as described in the section on the synthesis of quaternary ammonium halides was used as the monomer. A mixture of 10 g. of the monomer, 0.57 g. of water, and 0.17 g. of tertiary butyl hydroperoxide was placed in a beaker in the electric oven and held at 75° C. for 30 hours. After this period, the polymer was in the form of a sticky, brown, very viscous liquid, completely soluble in water. As

was true in the preceding compound, this polymer was unsuitable for ion exchange.

Allyl, cis 3-Chloroallyl Morpholinium Bromide.— The crude quaternary ammonium halide was polymerized in this experiment. A mixture of 10 g. of the monomer, 0.57 g. of water, and 0.17 g. of catalyst was held at 75°C. for 30 hours. Results similar to those obtained in the two preceding compounds were observed; i.e., the polymer was water-soluble.

Allyl, 2-Chloroallyl Piperidinium Bromide.— Polymerization of this compound was carried out at 65° and 30° C., using the proportions of water and catalyst stated above, for periods of 30 hours and 7 days, respectively. As in the previous examples, a water-soluble polymer was obtained.

Butyl, Diallyl, trans 3-Chloroallyl Ammonium Chloride.— This compound was mixed with water and tertiary butyl hydroperoxide in the proportions described previously and polymerized at 75° and 30° C. for periods of 24 hours and 7 days, respectively. These polymers showed solubility in water, but to a lesser extent than that encountered in experiments involving compounds with only two double bonds. These resins were unsuitable for ion exchange.

Triallyl, 2-Chloroallyl Ammonium Bromide.— Ten grams of this monomer, 0.57 g. of water, and 0.17 g. of tertiary butyl hydroperoxide were mixed and maintained at 30°C. for 10 days. At the end of this period, the soluble substances were leached out with water, giving a granular resin. This resin was then washed repeatedly with distilled

water to remove the last traces of the monomer. The final washings showed no test for the bromide ion when treated with silver nitrate. The polymer was dried under vacuum (4-5 mm.) for 24 hours and weighed. The volume occupied by the total quantity of resin was measured in the dry and wet conditions. A total of 4.3 g. of dry resin was collected, representing a yield of 43%.

Volume Occupied by 4.3 g. of Resin:

Dry..... 12.0 ml.

Wet..... 22.0 ml.

Coefficient of Swelling..... 1.83

[Volume Wet ÷ Volume Dry]

Tetrallyl Ammonium Bromide.— [See "Effect of Temperature," below.]

2. Effect of Temperature

Tetrallyl ammonium bromide was the subject of this study, using 10 g. samples mixed with water and catalyst in the percentages by weight of 93.1 of the quaternary, 5.3 of water, and 1.6 of catalyst.

Polymerization at 65°C.— The polymerization mixture was maintained at 65° in the electric oven for 24 hours. The resulting polymer was light brown in color. The solid mass was broken up by leaching out the soluble materials with water, resulting in a granular solid. This solid was washed with distilled water until the bromide ion could not be detected in the washings, indicating that the monomer had been removed. The resin

was then dried in a vacuum desiccator overnight and weighed. The volume of the resin was measured in both dry and wet conditions. A total of 6.55 g. of polymer was collected, a yield of 65.5%.

Volume Occupied by 6.55 g. of Resin:

Dry..... 12.1 ml.

Wet..... 23.1 ml.

Coefficient of Swelling..... 1.91

Polymerization at 40°C.— The reaction mixture was held constant at 40° in a water bath for 36 hours. At the end of 3 hours the mixture had become solid. The resin was broken up with water and washed as described previously. After drying in the vacuum desiccator, weight and volume measurements were made as before. A total of 7.70 g. of polymer was obtained, representing a yield of 77.0%.

Volume Occupied by 6.9 g. of Resin:

Dry..... 14.5 ml.

Wet..... 18.3 ml.

Coefficient of Swelling..... 1.26

Polymerization at 30°C.— The polymerization mixture was allowed to react at 30° for 7 days. The resulting resin was then purified and dried as outlined above. A total of 6.55 g. of resin was obtained, giving a yield of 65.5%.

Volume Occupied by 6.41 g. of Resin:

Dry..... 19.0 ml.

Wet..... 22.2 ml.

Coefficient of Swelling..... 1.17

Polymerization at 23°C.— This polymerization was carried out by allowing the usual mixture of reactants to stand at constant temperature for 14 days. After this period, the resulting resin was purified and dried as before. The yield was 7.70 g., or 77.0% of the theoretical.

Volume Occupied by 7.3 g. of Resin:

Dry..... 15.0 ml.

Wet..... 17.0 ml.

Coefficient of Swelling..... 1.13

2. Emulsion Polymerization

A simple emulsion system was used, consisting of a solution of the monomer in water, the catalyst, a dispersion medium, and an emulsifying agent. Ten grams of benzene, 10 g. of tetrallyl ammonium bromide, 10 g. of water, and 0.4 g. of Aquarex D[a] were mixed in a 200 ml., three-necked flask equipped with a mechanical stirrer. Stirring was begun and the mixture brought to a constant temperature of 60°C. Then 0.17 g. of catalyst was added to the mixture, and the reaction continued for 30 hours. The emulsion was cooled and saturated with sodium chloride to precipitate the polymer. The product was thoroughly washed with distilled water and dried overnight in the vacuum desiccator. A very fine powder was obtained in low yield — 0.8 g., or 8.0% of the theoretical.

Volume Occupied by 0.8 g. of Resin:

Dry..... 1.40 ml.

Wet..... 1.55 ml.

Coefficient of Swelling..... 1.11

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[a]An emulsifying agent produced by E. I. du Pont de Nemours and Company.

4. Suspension Polymerization Using Benzene

In this reaction, the same proportions of monomer (tetrallyl ammonium bromide), water, and catalyst were used as in the bulk polymerization experiments on the preceding pages. This mixture was placed in a 200 ml., three-necked flask with 10 ml. of benzene and stirred mechanically at a constant temperature of 60°C. for 12 hours. At the end of this time, gelation had occurred. The gel was broken up and leached with water. The benzene was removed by evaporation prior to washing the resin and drying at 105°C. A total of 3.80 g. of product was recovered, representing a yield of 38.0%.

Volume Occupied by 3.8 g. of Resin:

Dry..... 8.0 ml.

Wet.....41.0 ml.

Coefficient of Swelling..... 5.1

5. Suspension Polymerization Using Ethyl Benzene

This polymerization system was employed at two temperatures, 70° and 40° C. The proportions of constituents were the same in each case.

Polymerization at 70°C.— Ten grams of tetrallyl ammonium bromide, 5 g. of water, and 50 ml. of ethyl benzene were heated to 70° while stirring at a uniform rate. The stirring rate was regulated before the addition of the catalyst so that the monomer was broken up into small globules, then held at this rate, uninterrupted, throughout the reaction. After the selected temperature was reached, 0.17 g. of catalyst was added, and

the reaction continued for 2½ hours. At the end of this time, the polymer was filtered, washed with acetone and water, and dried under vacuum. Although some irregular particles of resin were obtained, a large proportion of the polymer was in the form of pearls. A yield of 8.70 g., or 87.0%, was obtained.

Volume Occupied by 8.70 g. of Resin:

Dry..... 13.0 ml.

Wet..... 23.0 ml.

Coefficient of Swelling..... 1.77

Polymerization at 40°C.— The same general procedure was used as described in the preceding system. The mixture was stirred uniformly and allowed to react at 40° for 48 hours. The resulting polymer was washed with acetone and water, then dried under vacuum. As was true in the case above, a large proportion of the polymer was in the form of pearls. A total of 8.60g. of resin was recovered, a yield of 86.0%.

Volume Occupied by 8.60 g. of Resin:

Dry..... 18.0 ml.

Wet..... 27.5 ml.

Coefficient of Swelling..... 1.53

TABLE IV

PROPERTIES OF ION EXCHANGE RESINS

Monomer	Method of Polymerization	Temperature, °C.	Swelling Coefficient[a]	Yield, %	Capacity		Wt. Resin per Ml. Wet
					MEQ/Ml.	MEQ/g.	
Triallyl, 2-Chloroallyl Ammonium Bromide	Bulk	30	1.83	43.0	0.405	2.08	0.195
Tetraallyl Ammonium Bromide	Bulk	65	1.91	65.5	0.640	2.24	0.284
Tetraallyl Ammonium Bromide	Bulk	40	1.26	77.0	0.523	1.39	0.377
Tetraallyl Ammonium Bromide	Bulk	30	1.17	65.5	0.450	1.53	0.289
Tetraallyl Ammonium Bromide	Bulk	23	1.13	77.0	0.432	1.01	0.430
Tetraallyl Ammonium Bromide	Emulsion	60	1.11	8.0	...	..	0.52
Tetraallyl Ammonium Bromide	Suspension[b]	60	5.1	38.0	...	..	0.093
Tetraallyl Ammonium Bromide	Suspension[c]	70	1.77	87.0	0.664	1.68	0.378
Tetraallyl Ammonium Bromide	Suspension[c]	40	1.53	86.0	0.773	1.98	0.312

[a]Volume Wet ÷ Volume Dry. [b]In Benzene. [c]In Ethyl Benzene.

Section V

ION EXCHANGE CAPACITY OF RESINS

A. General Considerations

The capacity of resins to exchange anions may be determined in a variety of ways, since no standard method of evaluation has been adopted. One of the most satisfactory methods involves the titration of a known quantity of the hydroxyl form of the resin with standard acid. This method leads to results that show graphically a close resemblance to titration curves of the strong base-strong acid type. The titration technique was used in this work. The unit of resin selected for the titration may be the dry weight of the halide form, the settled volume of the wet hydroxyl form, or the tamped volume of the hydroxyl form — all give different values of capacity. The unit of resin chosen for this research was the settled volume of the wet resin; the capacity was expressed in milliequivalents of anion exchanged per milliliter of wet resin. The capacity was also computed in milliequivalents of anion per dry weight of unconverted resin (the halide form), since this unit has a closer correlation with the cost of the resin.

Heating of quaternary ammonium salts leads to a certain amount of degradation to tertiary amines. This degradation can occur during the course of the polymerization, if the temperature is elevated. For this reason, some tertiary amine groups are often present in the polymer, along with the quaternary groups. These amine groups are capable of anion exchange but at a pH lower than that of the quaternary groups. Although

this amine capacity may be measured by means of the technique used herein, this factor was neglected, since comparatively little degradation occurred at the low temperatures used and the resulting amine capacity was small. Evidence of slight thermal degradation may be observed as an irregularity in titration curves shown on the accompanying graphs.

The method of determining anion exchange capacity herein is one in use in industrial laboratories.[a] It consists of titrating a measured volume of the converted resin (hydroxyl form) with standard acid, using a pH meter for measurement of anion concentration.

For the titration, the resin was first converted from the original form to the hydroxyl form by washing with normal sodium hydroxide. This exchange may be illustrated by the following equation:

$$(R_4NBr)_n + n\ NaOH \longrightarrow (R_4NOH)_n + n\ NaBr$$

As may be seen from this equation, a measure of the progress of the conversion may be obtained by testing the effluent for bromide ion with silver nitrate. This test was performed at intervals until the acidified effluent showed less than 10 parts per million of bromide ion. The value of 10 parts per million was selected arbitrarily, since the concentration of the bromide ion in the effluent approached zero asymptotically [see Section VI].

Conversion was accomplished through a column (2 x 40 cm.) with a 50-mesh metal screen fixed 4 cm. from the bottom. An overflow tube

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[a] Private communication from the National Aluminate Corporation, Chicago, Ill.

was passed up from the bottom of the column in an elongated "S" curve so that the exit end was always above the top of the resin bed. This overflow tube was used in order to keep the liquid level above the resin at all times, since the hydroxyl form of the resin is unstable when dry.[5] Addition of the sodium hydroxide was carried out through a one-liter addition funnel securely stoppered in the top of the column.

After conversion was complete, as evidenced by the low halogen content of the effluent, the resin was washed free of excess sodium hydroxide by passing distilled water through the column until the effluent no longer gave a color change with phenolphthalein. The wet resin was then removed from the column and stored under water until used.

The converted resin was allowed to settle until no further volume change occurred, and a standard volume was then removed. This sample was placed in a beaker equipped with a mechanical stirrer and pH meter electrodes. Potassium chloride solution of a known concentration was added and the titration begun. The resin was titrated with normal hydrochloric acid, added in increments of one milliliter at intervals of 3 minutes. The pH was read just prior to each addition of acid. The reaction in the resin is shown below:

$$(R_nNOH)_n + n\,KCl \longrightarrow (R_nNCl)_n + n\,KOH$$

The capacity of each resin was computed by dividing the number of millimoles of acid required to give the titration break by the volume of resin used.

It may be argued that the time interval of 3 minutes allowed for equilibrium to be reached during the titration was insufficient. However, the conversion from the hydroxyl form of the resin to the chloride form under these conditions was found to occur at a speed usually attributed to ionic reactions. Some evidence of this speed may be found in a later section [see Section VI].

B. Experimental

Measurement of the pH in these titrations was made by means of a Beckman Model H-2 pH Meter, using the Beckman #4990 glass electrode and the Beckman #4970 calomel electrode. The instrument was standardized against a buffer solution just prior to each titration.

The hydrochloric acid used in these titrations was standardized against standard sodium hydroxide solution. Approximately one normal acid was used. A 0.4 N potassium chloride solution was prepared by accurately weighing the salt and making up the solution in a volumetric flask. In order to adjust the initial concentration of the chloride ion in the titration mixture, a measured volume of this stock solution was diluted to the proper volume. An initial concentration of 0.01 N chloride ion was used in all titrations except the experiments in which this concentration was the only variable [p. 45].

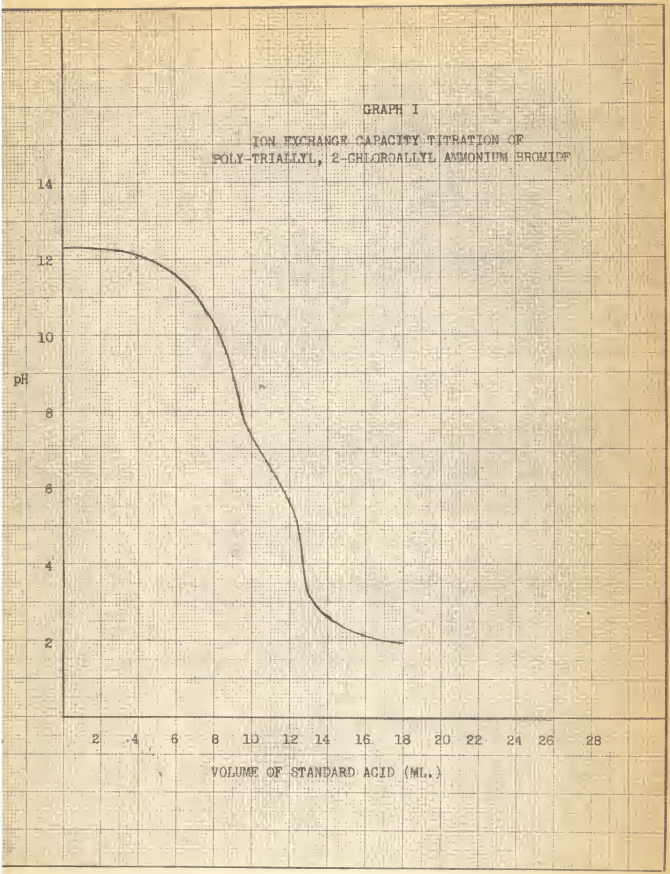
The details of the titrations were simple. Twenty-two milliliters of the wet resin was placed in the titration beaker, equipped with stirrer and electrodes. The potassium chloride solution was then

added and the time of addition observed. After 3 minutes, the pH was recorded and the first milliliter of acid added at once from the buret. A second 3-minute interval was allowed to pass, and the pH was determined again. This routine of addition and measurement of pH was continued until the titration was completed. The results of the ion exchange capacity titrations carried out in this investigation are shown in Graphs I - IV.

A study of the effect of the initial concentration of the chloride ion on the capacity of the resin was carried out. Previous work of this sort was done by Kunin and McGarvey.[15] The concentrations chosen for this study were zero, 0.001N, 0.01 N, and 0.1 N. All factors except this initial concentration were held constant. The results of this work are shown in Graph V.

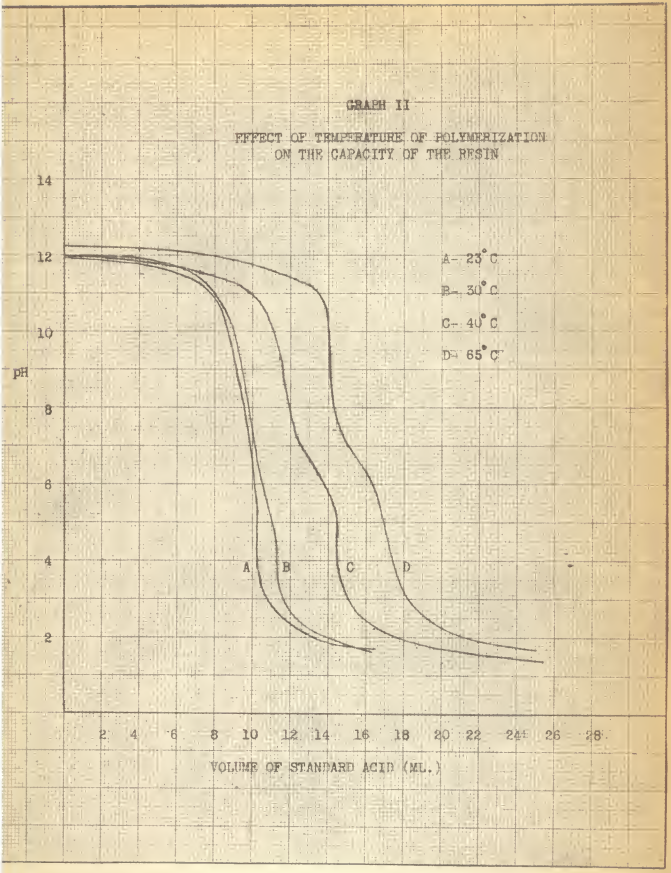
GRAPH I

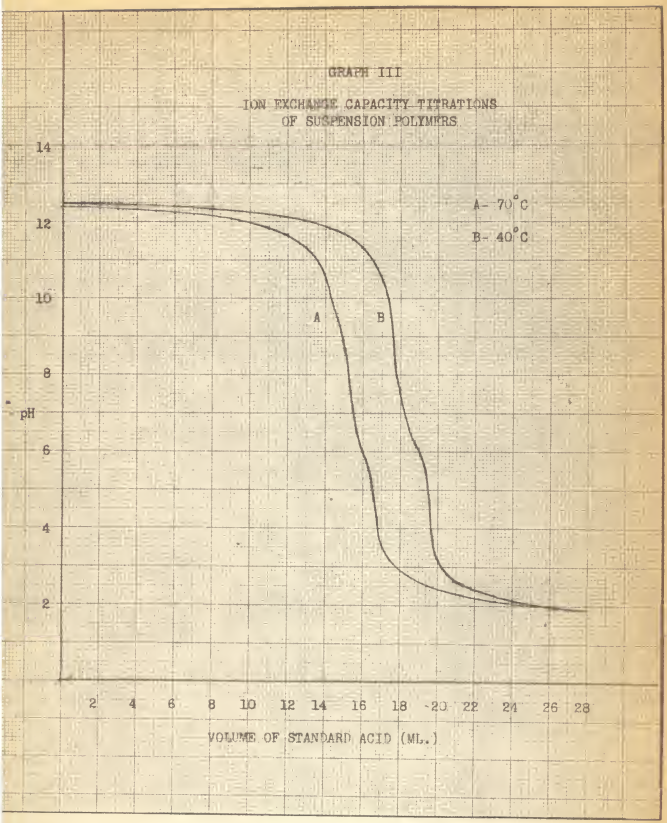
ION EXCHANGE CAPACITY TITRATION OF
POLY-TRIALLYL, 2-CHLOROALLYL AMMONIUM BROMIDE

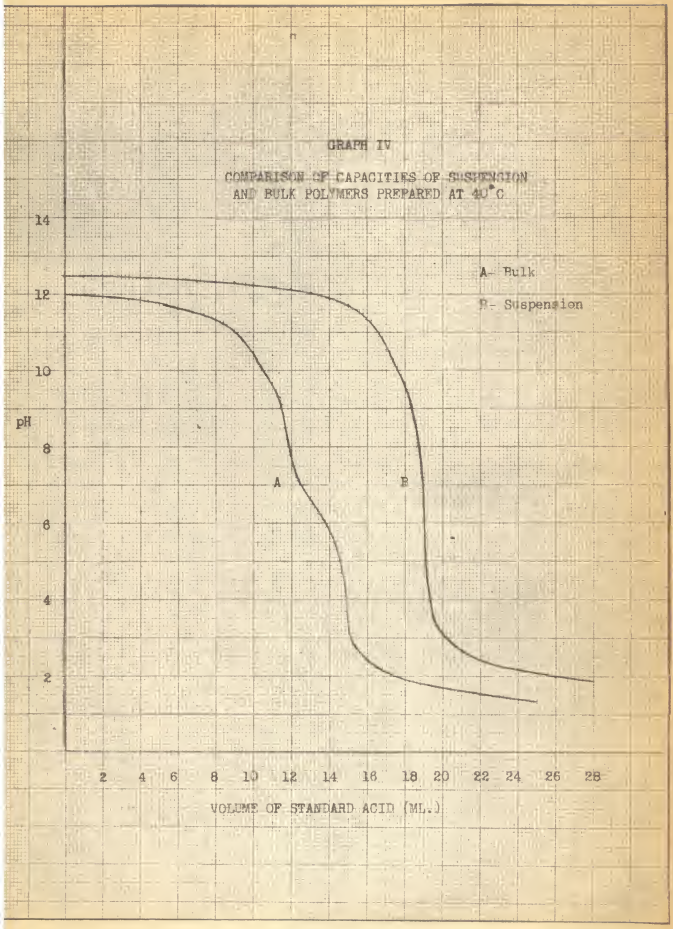


GRAPH II

EFFECT OF TEMPERATURE OF POLYMERIZATION ON THE CAPACITY OF THE RESIN

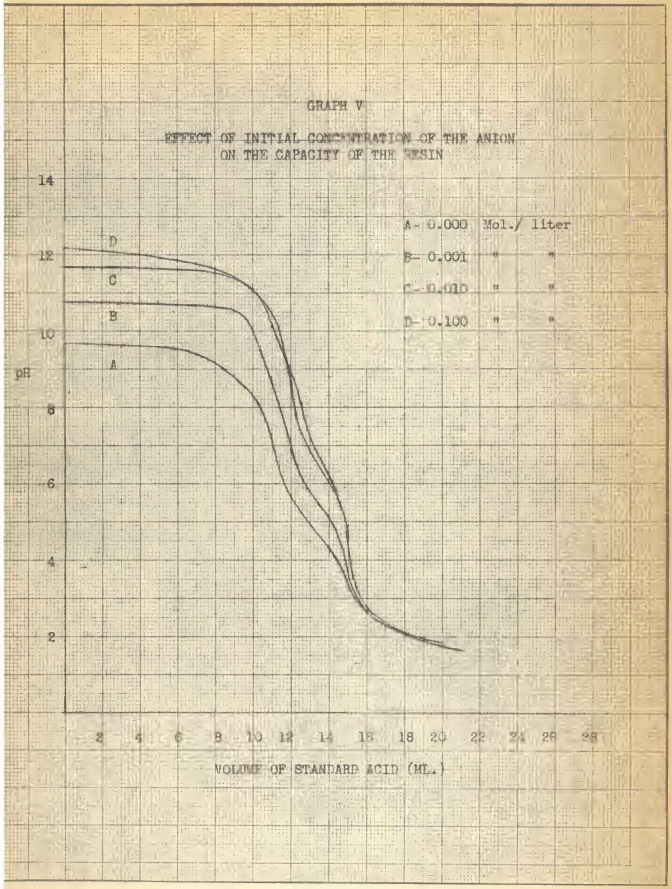



GRAPH III
ION EXCHANGE CAPACITY TITRATIONS
OF SUSPENSION POLYMERS
A- 70°C
B- 40°C
A
B
pH
14
12
10
8
6
4
2
2 4 6 8 10 12 14 16 18 20 22 24 26 28
VOLUME OF STANDARD ACID (ML.)


GRAPH IV
COMPARISON OF CAPACITIES OF SUSPENSION AND BULK POLYMERS PREPARED AT 40°C
A- Bulk
B- Suspension
pH
14
12
10
8
6
4
2
A
B
2 4 6 8 10 12 14 16 18 20 22 24 26 28
VOLUME OF STANDARD ACID (ML.)

GRAPH V

EFFECT OF INITIAL CONCENTRATION OF THE ANION ON THE CAPACITY OF THE RESIN



Section VI

RATE OF ION EXCHANGE OF RESINS

A. General

The rate of ion exchange of resins is of considerable importance both industrially and experimentally. In industrial applications, this rate must be known in order to calculate the time of contact necessary between solution and resin to give maximum efficiency. Experimentally, some knowledge of this rate is important in the determination of the capacity of resins so that sufficient time may be allowed for equilibrium to be reached during the titration.

With these applications in mind, an attempt was made to study the kinetics of anion exchange of a typical resin produced in this research. This study was made on the replacement of hydroxyl ions by chloride ions in a standard concentration of the anion. A known volume (22 ml.) of the hydroxyl form of the resin was stirred in solution with the selected concentration of chloride ion and hydrochloric acid for a measured interval of time, and an aliquot portion of the solution titrated for excess acid with standard sodium hydroxide. A separate sample was used for each time interval. It was found from this study that, within the limits of experimental error, no difference in the number of hydroxyl ions replaced occurred over a fairly long interval of time. Equilibrium must have been reached quite rapidly.

As was mentioned before, it was known that the concentration of halide ions in the effluent from the column became asymptotic during the conversion of the resin to the hydroxyl form. For this reason, determination of the quantity of normal sodium hydroxide necessary to reach this point of slow change in exchange of ions seemed important. A study was made of the relationship between the volume of effluent passed and the concentration of halide ion in the effluent. As a corollary to this experiment, the reverse change (from hydroxyl form to halide form) was studied.

B. Experimental

A sample of resin produced from the bulk polymerization of tetrallyl ammonium bromide at 65°C. was used for this kinetics study. The resin was converted to the hydroxyl form by the method described previously and washed free of excess hydroxyl ion. Three 22 ml. samples of the wet resin were mixed with water in 250 ml. volumetric flasks and the solutions adjusted to 0.01 molar in KCl and 0.20 molar in HCl. These concentrations were selected to represent the ultimate concentrations found in the titration of the resins. The mixtures of resin and solution were stirred mechanically in three 500 ml. flasks. The reactions were stopped at the end of 2 minutes, 3 hours, and 48 hours, respectively, by rapid filtration of the resin. Aliquots were withdrawn from the filtrates, and the excess acid present was titrated with standard sodium hydroxide, using phenolphthalein as the indicator. Based upon the known

weight of dry bromide form of the resin, it was known that 24.4 millimoles of quaternary groups were present in each sample. From this information, the percentage conversion of each sample to the halide form was calculated, since each hydrogen ion which had been used up represented one hydroxyl ion released. The data are tabulated below:

Sample Number	Time	Conversion, %
1	2 min.	71.5
2	3 hrs.	71.0
3	48 hrs.	70.3

It was believed that these values varied only within the limits of experimental error, indicating that the reaction probably reached equilibrium in two minutes or less.

For the experiment conducted to determine the amount of halide ion necessary for practically complete conversion of the resin, the sample of tetrallyl ammonium bromide polymerized in suspension with ethyl benzene at 70°C. was used. This sample (8.7 g. in the bromide form, 23 ml. wet) was first converted to the hydroxyl form by means of the usual method in the column already described. The resin formed a column about 14 cm. in height. After washing, the resin was drained, but not dried. Potassium chloride solution (1.00 normal) was then allowed to flow through the resin, maintaining a constant rate of 13.5 ml. per minute. A total of twenty consecutive samples of the effluent were collected, the first eighteen, of 25 ml. each, and the last two, of 100 ml. volume. Ten

milliliter aliquots of each sample were titrated in duplicate for free hydroxyl ion, using standard hydrochloric acid. Methyl red was used as the indicator. As may be observed from a study of Graph VI, conversion proceeded very rapidly during the passage of the first 150 ml. of potassium chloride solution, reaching a hydroxyl ion concentration of 0.0026 moles per liter. The conversion thereafter was much slower, since the last sample collected (after 650 ml. had passed) showed a concentration of approximately 0.001 moles per liter. The dotted portion of the graph represents the effect of the dilution of the first effluent by the small amount of water which did not drain from the resin.

The corresponding conversion from the chloride form to the hydroxyl form of the resin was conducted, using the same sample, in situ. Complete conversion to the chloride form was assured by washing the resin with 6 N HCl, and then with water. After all free chloride ions had been washed out, the resin was air dried, using an aspirator. To effect the conversion, normal sodium hydroxide solution was passed through the resin at a constant rate of 5.0 ml. per minute. Eighteen consecutive 25 ml. samples of the effluent were collected, followed by one sample of 125 ml., two of 100 ml. each, one of 225 ml., and the final, 25 ml. A total volume of 1025 ml. of effluent was collected in these twenty-three samples. Aliquots of these samples were acidified with nitric acid and analyzed gravimetrically for the chloride ion. As may be seen from Graph VI, the rate of exchange was not so rapid as that found in the reverse reaction. Between 650 and 700 ml. of alkali was

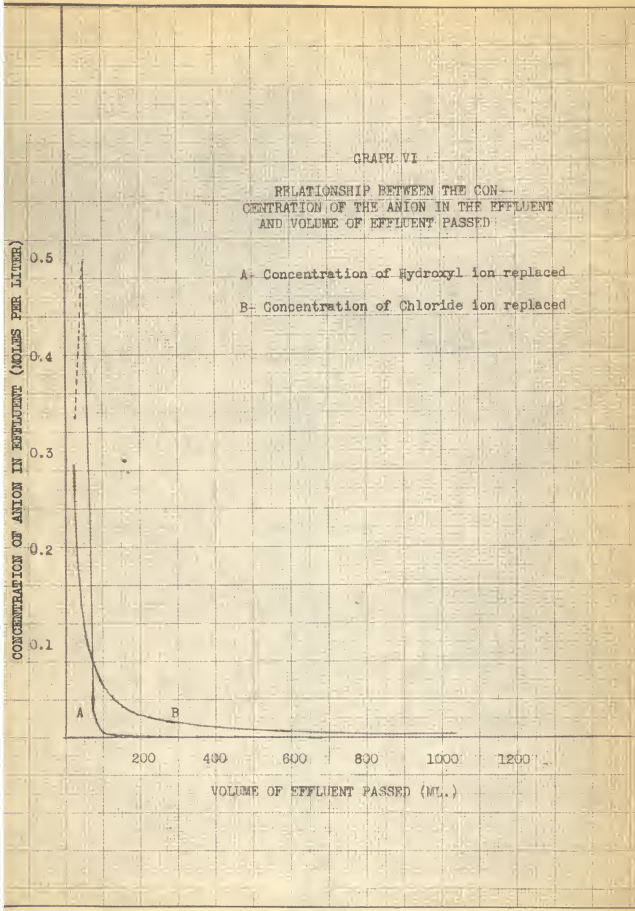
necessary to bring the chloride ion concentration in the effluent to a reasonably constant value. The concentration of chloride ion in the effluent after 650 ml. had passed was about 0.006 moles per liter. After 1025 ml. had passed, the concentration was reduced to about 0.004 moles per liter.

GRAPH VI

RELATIONSHIP BETWEEN THE CONCENTRATION OF THE ANION IN THE EFFLUENT AND VOLUME OF EFFLUENT PASSED

A- Concentration of Hydroxyl ion replaced

B- Concentration of Chloride ion replaced



Section VII

EVALUATION OF RESINS

In the main, two criteria were used in the evaluation of the polymers produced in this research: The relative solubility of the product (as indicated by the coefficient of swelling) and the ion exchange capacity of the product. Within a limited range of solubility, the ion exchange capacity was considered the more important measure of quality. However, it was realized that in those cases in which swelling was significant, the capacity was affected, since the number of moles of active exchange groups varied for a given volume of wet resin. Furthermore, extreme swelling of the resins led to great difficulty in manipulation.

The swelling tendencies of all resins prepared are listed in Table IV [p. 40]. It may be seen from this table that reduction in the temperature of the polymerization gave a progressive increase in the amount of crosslinking [i.e., a decrease in swelling] in the resins. Slightly more crosslinking was found with the resin polymerized in bulk at 40°C. than with the resin produced in suspension at the same temperature. The emulsion polymerization gave the resin with the highest degree of crosslinking, having a coefficient of swelling of 1.11. However, the yield in this reaction was low, and the extremely fine particle size made this resin impractical. The suspension polymerization in benzene led to a resin extremely difficult to manipulate, since its swelling coefficient was 5.1.

Ion exchange capacity determinations were made on all resins except those produced by emulsion polymerization and suspension polymerization in benzene. The two samples polymerized in ethyl benzene suspension showed the highest ion exchange capacity per unit volume. These samples would probably be the most useful commercially where the volume of the resin bed is limited — an important factor in some industrial applications. On the other hand, the polymers showing the highest values of ion exchange capacity per unit weight (poly-triallyl, 2-chloroallyl ammonium bromide and poly-tetraallyl ammonium bromide polymerized in bulk at 65°C.) would represent less expensive materials.

Two other considerations of the quality of the resins may be discussed here: namely, the hardness of the resin particle and the uniformity of particle size. A hard resin particle is desirable, since continued washing has the effect of powdering material which is too soft. Uniform particle size is necessary to promote ease of handling and speed of washing. Of the resins produced in this research, the ones showing the best qualities of hardness and uniformity of size of particle were the two samples polymerized in suspension with ethyl benzene.

A compilation of the properties of all ion exchange resins studied herein may be found in Table IV.

Section VIII

METHODS OF ANALYSIS

All tertiary amines were analyzed for nitrogen by means of the Kjeldahl method, using mercuric oxide for the catalyst. Carefully weighed samples of the amines were digested in a mixture of 25 ml. of concentrated sulfuric acid, 10 g. of potassium sulfate, and 1.2 g. of mercuric oxide. Digestion of the sample was carried out over a period of 4-5 hours after the disappearance of color. This digestion was begun at a temperature well below boiling until the sample changed from black to dark brown in color and then was heated vigorously until digestion was complete. The samples were then cooled and diluted with 200 ml. of water. After adding 100 ml. of 40% sodium hydroxide (5% in sodium thiosulfate), the liberated ammonia was distilled into a measured volume of standard acid. The excess acid was titrated with standard sodium hydroxide, using methyl red as the indicator. The data resulting from these analyses may be found in Table II [p. 19].

Quaternary ammonium halides were analyzed by titration of the halide ion with 0.1 N silver nitrate. The weighed sample of the quaternary was dissolved in water and mixed with a small amount of dextrin [to prevent coagulation of the silver halide]. Dichlorofluorescein was used as the indicator, the titrations being made until the first pink color appeared in the precipitated silver halide. Speed in weighing the quaternary halides was important, since most of these compounds were hygroscopic. The results of the analyses are listed in Table III [p. 28].

A few resins were analyzed for nitrogen by the Kjeldahl method, outlined on the preceding page, in order to prove that addition polymerization had occurred without a significant amount of decomposition. These analyses are tabulated below:

Compound	Temperature (°C.)	Nitrogen, % Theoretical	Observed
Poly-Tetrallyl Ammonium Bromide	30	5.44	5.33
Poly-Tetrallyl Ammonium Chloride	65	6.55	6.48
Poly-Tetrallyl Ammonium Bromide	65	5.44	5.45
Poly-Tetrallyl Ammonium Bromide	65	5.44	5.46

All of the compounds used in this sample determination were produced by the bulk method of polymerization.

Section IX

DISCUSSION OF RESULTS

Of the two methods employed herein for the preparation of unsaturated tertiary amines, the method described by Willson and Wheeler[20] was found to give higher yields, with fewer by-products. The yields obtained by this method, with a few exceptions, were above 60%. All of the amines prepared were colorless, mobile liquids when freshly prepared but soon turned yellow upon standing.

Considerable difficulty was encountered in some cases in crystallizing the quaternary ammonium halides prepared in this research. Those compounds containing a 3-chloroallyl group proved the most refractory. With one of these compounds, allyl,trans 3-chloroallyl morpholinium bromide, success was realized in obtaining enough crystalline material to analyze; however, all efforts to produce crystals of the cis isomer of this compound failed. No characterization of the cis isomer was made; its identity rested only upon the method of synthesis. The other quaternary ammonium compounds were white, crystalline solids, hygroscopic and with rather high melting points.

Since none of the unsaturated quaternaries having only two allyl groups or substituted allyl groups formed insoluble polymers, it is believed that three or four such groups are necessary to produce satisfactory crosslinking. From the standpoint of functionality, this was unexpected since compounds with a functionality of four [i.e., with two double bonds] should crosslink. No explanation of this anomaly can be offered.

As had been expected, reduction of the temperature of polymerization resulted in a noticeable increase in crosslinking of the polymers, as evidenced by the decreased tendency to swell when wet. However, this increase in crosslinking, with its corresponding increase in the weight of the resin per milliliter, resulted in a decrease rather than an increase in ion exchange capacity. An explanation of this phenomenon may be found in the fact that the molecules of the polymers with more extensive crosslinking were too closely packed to permit free migration of the anions within the resin particles. The advantages of low temperature polymerization were realized, however, when the ethyl benzene suspension polymerization experiments were carried out. In addition to giving resins of higher capacity than were obtained by bulk polymerization, this method produced much more uniform particles, leading to greater ease in manipulation. As an explanation of the higher capacities encountered with the suspension polymers, it is suggested that the inert medium may have left minute interstices in the resin particle, offering an increased area of migration for the anions.

Emulsion polymerization, under the conditions used, gave a low yield of very fine polymeric material, unsatisfactory for experimental study. Suspension polymerization, using benzene, gave a polymer with a very low degree of crosslinking, causing swelling to such an extent that the product was impossible to manipulate.

The introduction of chlorine-substituted groups in the monomers was found to offer no improvement on the quality of the resins. Furthermore, purification of these monomers proved difficult in some cases.

The study of the effect of varying the initial concentration of the anion in the titration mixture for ion exchange capacity determinations was significant. A small, but noticeable, increase in the capacity of the resin occurred when the initial concentration was changed from zero to 0.001 N, 0.01 N, and to 0.10 N. This increase in capacity might have been predicted on the basis of the law of mass action. In addition, a wide variation in the pH range of the resin was noticed. In view of these facts, it seems important that this initial concentration be specified in any standard method of determining ion exchange capacity.

From the study of the ion exchange rates in this research, it is believed that this exchange occurs at a speed usually attributed to ionic reactions. The titrations of the hydroxyl form of the resins with a strong mineral acid show graphically a great similarity to typical strong base-strong acid titrations.

Of the resins investigated in this research, the one showing the highest capacity and best physical condition was the ethyl benzene suspension polymer of tetrallyl ammonium bromide, polymerized at 40°C. This resin exhibited a capacity of 0.773 milliequivalents of anion per milliliter of wet resin. This value is almost twice as high as that previously obtained from poly-tetrallyl ammonium bromide. It is believed that this value compares quite favorably with the capacities of anion exchange resins now available.

Section X

SUMMARY

Six new halogenated, unsaturated quaternary ammonium halides were prepared. Five of these new compounds were characterized. The identify of the sixth compound was assumed on the basis of the means of preparation, since purification was not effected.

Nine new halogenated, unsaturated tertiary amines were prepared as intermediates. All of these compounds were characterized and physical constants determined. Eight of these amines were prepared by the reaction of the appropriate secondary amine with the alkyl halide in the presence of aqueous sodium bicarbonate. The remaining compound was prepared by the reaction of the alkyl halide with aqueous ammonium hydroxide.

The unsaturated quaternary ammonium halides were polymerized by means of tertiary butyl hydroperoxide. Those compounds containing two or three double bonds gave rise to thermoplastic polymers, but those containing four double bonds formed thermosetting polymers. The thermosetting polymers were found to be suitable for ion exchange.

A study of the effect of the temperature of polymerization on the ion exchange capacity of the resin was made, using tetrallyl ammonium bromide. The reduction in temperature gave an increase in cross-linking but a decrease in ion exchange capacity.

An investigation of the effect of the method of polymerization on the quality of the resin was conducted, using tetrallyl ammonium bromide. Emulsion polymerization and suspension polymerization in benzene gave unsatisfactory results. Suspension polymerization in ethyl benzene produced resins of high ion exchange capacity and of good physical properties. The resins so produced showed capacities much higher than those previously obtained by use of the same monomer.

A kinetics study of the anion exchange properties exhibited by one of these resins indicated that the rate of exchange was comparable to that usually attributed to ionic reactions.

This research has led to anion exchange resins that compare favorably in pH range and capacity with those now available.

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BIOGRAPHICAL ITEMS

Francis L. Ingley was born in Jacksonville, Florida, on December 9, 1921. He began his undergraduate work at the University of Florida in September, 1940.

Mr. Ingley was called to active duty in the Officers' Reserve Corps of the Army of the United States in August, 1943, and after thirty-three months of active duty was released to inactive status in May, 1946. He was awarded the degree of Bachelor of Science in Chemistry in June, 1947, and the degree of Master of Science in February, 1949, at the University of Florida.

The author has held positions with the United States Department of Agriculture (1939-40) and with the United States Department of Horticulture (1940-41, part-time). He has served as undergraduate assistant at the University of Florida for three years and as graduate assistant for one year. He was awarded a graduate fellowship in July, 1948, and a United States Naval Research Fellowship in September, 1949.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the Candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date June 5, 1950

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